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Anion-directed assembly: the first fluoride-directed double helix

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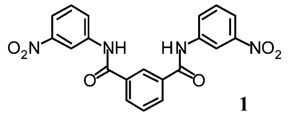
The crystal structures of anion complexes of two nitroaromatic functionalised isophthalamides are reported; the structures reveal assembly around anions in the solid-state and in the case of the fluoride complex of receptor 2, the formation of a double helix.

The use of anionic components to direct self-assembly processes is an area of supramolecular chemistry still in its infancy but one which is expanding the available non-covalent and coordinate bonding motifs for the construction of interlocked materials and new non-covalently linked molecular architectures.[1] For example, Lehn and co-workers have reported the synthesis of a circular helicate in which an iron complex cyclises around a chloride anion,[2] whilst Stoddart and co-workers[3] and Beer and co-workers[4] have reported examples of anion-assisted formation of non-covalent architectures using hexafluorophosphate and chloride respectively. Vögtle and co-workers[5] have used an anion templation approach to synthesise rotaxanes. Sessler and co-workers have shown that pyrrolic macrocycles containing appended carboxylate groups form anionic dimers[6] whilst in the inorganic arena, McCleverty, Ward and co-workers[7] and Mingos, Vilar and co-workers[8]and have used anions to direct the formation of new inorganic materials. In the solid state, Ward and co-workers have studied the factors influencing sulfonate–guanidinium-interactions[9] whilst Hosseini and co-workers have used amidinium–carboxylate interactions to assemble molecular rods, tapes and sheets.[10] We have recently reported the assembly of 2,5-diamidopyrrole anion dimers[11] and their use in the construction of anionic supramolecular polymers.[12] Anion templated helix formation is particularly rare with examples from de Mendoza and co-workers (sulfate directed helix formation by polyguanidinium strands)[13] and Kruger and co-workers (a chloride directed helix formed from pyridinium ligands.)[14] To the best of the authors' knowledge, there have been no reports of neutral synthetic ligands forming helices around anions, a surprising fact considering the considerable body of work amassed on amidic anion receptors over the last ten years[15] and the importance of amide groups in stabilising helical structures in proteins.[16] In this communication, we report the solid-state anion-directed assembly properties of two isophthalamide clefts including the first example of a helix formed by anion templation of an amide ligand.

The use of the isophthalamide skeleton as an anion receptor was pioneered by Crabtree and co-workers, with hosts forming complexes with fluoride and other anions.[17] Beer and co-workers have recently shown that the chloride complex of a pyridinium-3,5-diamide cation can be used to form self-assembled molecular architectures ('catenane precursors') with various hydrogen-bonded components.[4] Our interest in anion-directed self-assembly[11,12] led us to study the assembly properties of neutral isophthalamides containing electron withdrawing groups designed to enhance the ligand–anion interaction.

Compounds **1**[18] and **2** were synthesised by addition of 3-nitroaniline or 3,5-dinitroaniline to isophthaloyl dichloride in dry DMF affording the ligands in 41% and 39% respective yields. The fluoride binding properties of **1** and **2** were studied by ^1H NMR titration techniques in DMSO-d_6–0.5% water. During the titration, the amide NH protons disappear, however it is possible to follow shifts in the CH protons of the central aromatic ring. In the case of compound **1**, a complex NMR titration curve shows the presence of multiple equilibria in solution. Whilst with compound **2**, the CH resonance shifts upfield and plateaus at about one equivalent of fluoride. At higher fluoride concentrations, this proton continues to shift upfield. This data may be indicative of the formation of a 1:1 (or 2:2) fluoride:receptor complex at around one equivalent of fluoride which at higher fluoride concentrations presumably shifts to a 2:1 fluoride to receptor complex.



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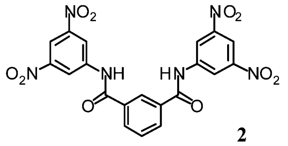

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We intended to study the fluoride complexes of both compounds **1** and **2** in the solid-state, however when compound **1** was crystallised from acetonitrile in the presence of excess tetrabutylammonium fluoride, crystals of the hexafluorophosphate salt were obtained (Fig. 1).†

In this structure, a PF_6 anion is located on a centre of inversion bound by two molecules of **1** *via* N–H···F hydrogen bonds: N3H···F = 2.806 Å, whilst N2 forms a bifurcated hydrogen bond (N2H···F1 = 3.186 and N2H···F2 = 2.807 Å) (Fig. 2).

Crystals of the tetrabutylammonium fluoride complex of **2** were formed by slow evaporation of an acetonitrile solution of the receptor in the presence of excess tetrabutylammonium fluoride.‡ The structure reveals a double helix formed around

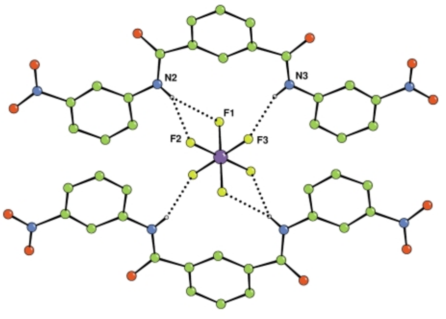

Fig. 1 The X-ray crystal structure of the tetrabutylammonium hexafluorophosphate salt of receptor **1**. Tetrabutylammonium counter cations and certain hydrogen atoms are omitted for clarity. Colour key: oxygen–red, carbon–green, nitrogen–blue, hydrogen–white, fluoride–yellow, phosphorus–purple.

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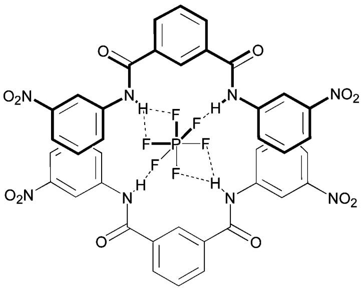

Fig. 2 The hydrogen bonding network in the crystal structure of the tetrabutylammonium hexafluorophosphate complex of receptor **1**.

two fluoride anions *via* NH···F^- hydrogen bonds, such that the N–F–N angles are N1···F1···N10 = 158.04° and N4···F2···N7 = 155.23° and the F^-–F^- separation is 3.716(6) Å (Figs. 3 and 4). This arrangement results in π–π interactions between the terminal nitroaromatic groups of 3.317(8) and 3.361(8) Å.

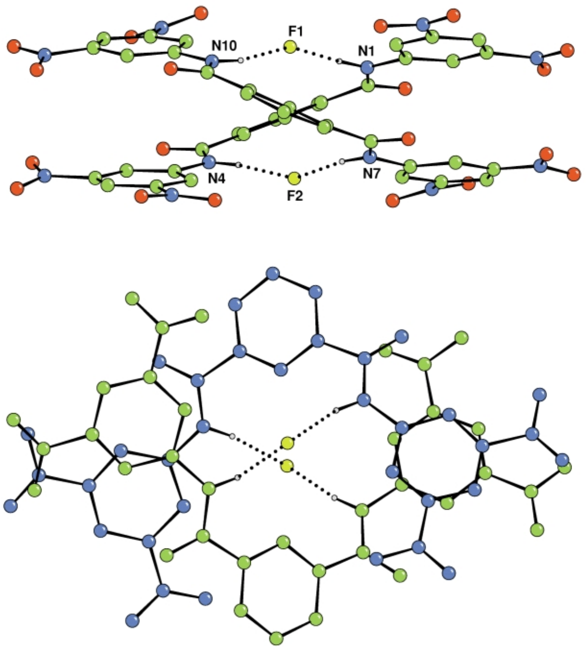

Fig. 3 Side view of the X-ray crystal structure of the fluoride complex of receptor **2** (above) and top view of the helix showing π-stacking interactions (below). Colour key (top structure): oxygen–red, carbon–green, nitrogen–blue, hydrogen–white, fluoride–yellow. Tetrabutylammonium counter cations and certain hydrogen atoms are omitted for clarity.

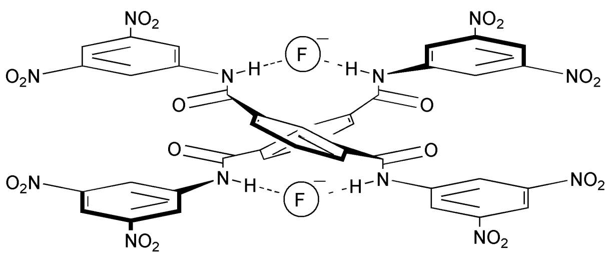

Fig. 4 The hydrogen bonding network present in the fluoride complex of **2**.

We have shown that very simple ligands such as **1** and **2** can form anion-assembled structures such as double helices in the solid state with the geometry of the anion determining the structure of the complex obtained. The use of anion geometry to control assembly and the role of π-stacking in the assembly of these complexes is currently being investigated in our research group. The results of these studies will be reported in due course.

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Notes and references

† Crystal data for $(\mathbf{1})_2$ TBA PF_6: $C_{72}H_{100}PF_6N_{10}O_{12}$, Mr = 1442.59, T = 120(2) K, triclinic, space group $P\bar{1}$, a = 11.4442(6), b = 12.3142(8), c = 13.2507(7) Å, α = 86.370(5), β = 85.797(4), γ = 78.520(2)°, V = 1822.82(18) Å^3, ρ_{calc} = 1.314 g cm^{-3}, μ = 0.12 mm^{-1}, Z = 1, reflections collected: 26306, independent reflections: 7951 (R_{int} = 0.0914), final R indices [$I > 2\sigma I$]: $R1$ = 0.0762, $wR2$ = 0.1676, Rindices (all data): $R1$ = 0.1616. $wR2$ = 0.2039. CCDC 197049. See http://www.rsc.org/suppdata/cc/b2/b210847j/ for crystallographic data in CIF or other electronic format.

‡ Crystal data for $(\mathbf{2}\text{-}F^-)_2$-2TBA$^+$: $C_{72}H_{96}F_2N_{14}O_{20}$, Mr = 1515.63, T = 120(2) K, monoclinic, space group $P2_1/c$, a = 18.9979(13), b = 22.1130(11), c = 17.9782(10) Å, β = 91.571(2)°, V = 7549.8(8) Å^3, ρ_{calc} = 1.333 g cm $^{-3}$, μ = 0.101 mm^{-1}, Z = 4, reflections collected: 17441, independent reflections: 9304 (R_{int} = 0.0696), final R indices [$I > 2\sigma I$]: $R1$ = 0.1121, $wR2$ = 0.2974, R indices (all data): $R1$ = 0.2200. $wR2$ = 0.3545. CCDC 197050. See http://www.rsc.org/suppdata/cc/b2/b210847j/ for crystallographic data in CIF or other electronic format.

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